REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE September 2008	3. REPORT TYPE AND DATES COVERED **Final Report** (August 2004 – September 2008)

4. TITLE AND SUBTITLE Diamond-Like and Self-Assembling Organic Nanostructures: Measurement and Simulation of Intermolecular Interactions and Structural Characteristics	5. FUNDING NUMBERS GRANT No. W911NF-04-1-0383
6. AUTHORS Thomas F. George, Lahsen Assoufid, G. Ali Mansoori and Guoping Zhang	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Missouri–St. Louis, St. Louis, MO; Argonne National Laboratory, Argonne, IL; University of Illinois at Chicago, Chicago, IL; Indiana State University, Terre Haute, IN	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME AND ADDRESS U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Our experimental and theoretical objectives have focused on adamantane, the first diamondoid. This compound gives us substantial detailed information about the interaction between carbon-carbon, carbon-hydrogen, and hydrogen-hydrogen atoms. This has provided a first test case for the theoretical teams at the University of Missouri–St. Louis and Indiana State University to accurately measure and compute the electronic structure and mechanical properties. The results have been compared with the existing model potentials, through which we have been able to systematically improve the quality of those potentials. Experimental intermolecular force measurements, positional assembly and applications of diamondoids as molecular building blocks have been carried out by the experimental teams at Argonne National Laboratory and University of Illinois at Chicago.

Over 30 publications have resulted from this work, including a book on *Molecular Building Blocks (MBBs) for Nanotechnology*, published in 2007 by Springer-Verlag. This book, edited by the principal investigators for this grant, consists of seventeen chapters covering all the important aspects of MBBs, including diamondoids and the relation of diamondoids with other MBBs.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Diamondoids, molecular building blocks, self-assembling, organic nanostructures, measurements, simulations, intermolecular interactions	
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	**UNCLASSIFIED**	**UNCLASSIFIED**	U

MEMORANDUM OF TRANSMITTAL

U.S. Army Research Office
ATTN: AMSRL-RO-BI (TR)
P.O. Box 12211
Research Triangle Park, NC 27709-2211

CONTRACT/GRANT NUMBER: W911NF-04-1-0383

REPORT TITLE: Diamond-Like and Self-Assembling Organic Nanostructures:(Measurement and Simulation of Intermolecular Interactions and Structural Characteristics).

2.c: **Final Progress Report**

(1)-(3) Optional - blank

(4) Statement of the problem studied

Our problem is to investigate the complicated structure-property relation of organic nanostructures at the nanoscale level by high-level materials simulation. A clear understanding of such a relation is extremely essential to designing functional molecular gears for micro-machines and sensitive bionanosensors. Diamondoids are excellent materials for this study.

(5) Summary of the most important results

Our theoretical investigations have progressed quite well, with the following results:

(i) Method characterization of diamondoids

Challenges to simulate nanostructured are obvious both theoretically and computationally. However, what is even more challenging is the selection of a reliable and workable theoretical method which can handle a wide range of mechanical properties of diamondoids. We have tested two different quantum chemical softwares, where one is Molpro and the other is Gaussian03. Molpro usually has faster performance than Gaussian03 for small systems at the Hartree-Fock level, but uses too much disk space and memory for a large system. We have found Gaussian03 to be more appropriate for adamantane. We have discovered that the Hartree-Fock method gives a correct molecular symmetry but a very poor mechanical property. We have found that the density functional theory at the B3LYP level gives a much better result. This is also consistent with all the previous theoretical and experimental investigations.

(ii) First-principles simulation of the interaction between adamantane and an atomic-force-microscope tip

Here we have used the first-principles calculation to investigate the interaction between adamantane and an atomic-force-microscope tip. By holding the tip at different distances from adamantane, three scans across two surfaces – one with a carbon atom at the center and the four other equivalent atoms at the corners, and the other with three equivalent carbon atoms in the front and three other atoms in the back forming a hexagon shape – reveal the detailed morphology of adamantane. For the first scanned surface, a huge potential energy change is observed when the tip is close to adamantane, which results from the strong interaction from two hydrogen atoms attached to the center carbon atom. On the second scanned surface, a radial scan shows a maximum force constant of 2 Hartrees/$Å^2$. This is proof of the hardness of adamantane. The rotational scan along the second surface reveals a systematic change in the potential energy as the tip is moved away from adamantane. Due to the existence of two types of carbon atoms in adamantane, the original potential maxima are shifted 60° to new maxima. Between these maxima, there is a flat region. Finally, an x-y force scan over the above two surfaces is performed, where two distinctive images of hydrogen atoms are found. These results are detectable experimentally.

(iii) Chemical modification of adamantane structure

Motivated by a recent investigation showing that the nitrogen vacancy (NV) in diamond is magnetic (where one removes one carbon atom and replace another carbon atom by a nitrogen atom), we have investigated the possibility of whether nitrogen-modified adamantane shows magnetic properties, We have found that for a single NV, adamantine is not magnetic. This is true irrespective of which pair of carbon and vacancy is created. However, the gap between the magnetic and nonmagnetic ground states is quite small. This result suggests that in a thermal activated situation, the chemically-modified adamantane might show the magnetic properties. This could be useful as a magnetic and thermal sensor.

Our experimental stuidies have progressed well and are still underway as follows:

(iv) Optoelectronic behavior of diamondoids molecules

Diamondoids have been of great interest in recent years due to their role in nanotechnology, drug-delivery and medicine. Due to their six or more linking groups, they have found major applications as templates and as molecular

building blocks in nanotechnology, polymers synthesis, drug delivery, drug targeting, DNA-directed assembly, DNA-amino acid nanostructure formation, and in host-guest chemistry. In this project, the molecular nature of diamondoids, their molecular specificities, their intermolecular interactions and their opto-electronic properties have been studied in a combined experimental-theoretical effort. These studies are aiding in our understanding of the structure-property relations and self-assembly of diamondoids, which is essential for designing functional molecular gears for micro- and nano-electro-mechanical systems (MEMS and NEMS) and sensitive bionanosensors, and for developing new nanodrugs, just to name a few. The experimental investigations on this subject have been utilizing the facilities of the Center for Nanoscale Materials of Argonne National Laboratory.

(6) Bibliography (publications acknowledging ARO support)

1. G. A. Mansoori, T. F. George, L. Assoufid and G. P. Zhang, Editors, *Molecular Building Blocks for Nanotechnology: From Diamondoids to Nanoscale Materials and Applications* (Springer, New York, 2007), *Topics in Applied Physics*, Volume **109**, 440 pages.
2. G. P. Zhang and T. F. George, "Controlling Vibrational Excitations in C_{60} by Laser Pulse Durations," *Physical Review Letters* **93**, 147401 (2004).
3. R. Divan, D.C. Mancini, Q. Ma, R.A. Rosenberg, L. Assoufid and X. M. Lin, "Deposition of Metallic Nanoparticles from Solution using Synchrotron Radiation," *Papers of the Joint Users Meeting for the Advanced Photon Source and Center for Nanoscale Materials* (Argonne National Laboratory, May 2-6, 2005).
4. L. Assoufid, G. A. Mansoori, T. F. George and G. P. Zhang, "Diamondoids as Molecular Building Blocks for Nanotechnology," *Proceedings of the International Congress of Nanotechnology 2005*, held in San Francisco (International Association of Nanotechnology, Inc., Sacramento, CA, 2005), 16 pages.
5. S. Li, T. F. George and X. Sun, "Charge Flipping of Spin Carriers in Conducting Polymers," *Journal of Physics: Condensed Matter* **17**, 2691 (2005).
6. G. Tóth, K. Kordás, J. Vähäkangas, A. Uusimäki, T. F. George and L. Nánai, "Laser-Induced Gold Deposition on p^+-Si from Liquid Precursors: A Study on the Reduction of Gold Ions Through Competing Dember and Seebeck Effects," *Journal of Physical Chemistry B (Letters)* **109**, 6925 (2005).
7. K. Kordás, G. Tóth, J. Levoska, M. Huuhtanen, R. Keiski, M. Härkönen, T. F. George and J. Vähäkangas, "Room Temperature Chemical Deposition of Palladium Nanoparticles in Anodic Aluminum Oxide Templates," *Nanotechnology* **17**, 1459-63 (2006).
8. S. Li, S. Wang, X. Sun, Z. J. Wang and T. F. George, "Light Pulse Propagation in Disordered Thin Films and Mode Selection for Random Lasers," *Applied Physics Letters* **88**, 111103 (2006).
9. A. K. Popov, R. S. Tanke, J. Brummer, G. Taft, M. Loth, R. Langlois, A. Wruck and R. Schmitz, "Laser-Stimulated Synthesis of Large Fractal Silver Nanoaggregates," *Nanotechnology* **17**, 1901 (2006).
10. T. F. George and P. H. Handel, "Quantum 1/*f* Effect Based on Quantum Information Theory," *International Journal of Modern Physics B* **20**, 1343 (2006).
11. G. P. Zhang, "Optical High Harmonic Generation in C_{60}," *Physical Review Letters* **95**, 047401 (2005).
12. G. P. Zhang and T. A. Callcott, "Resolving *dd* Transitions in NaV_2O_5 Using Angle-Resolved Resonant Inelastic X-Ray Scattering at the V *L* Edge," *Physical Review B* **73**, 125102 (2006).
13. S. Li, T. F. George, L. S. Chen, X. Sun and C. H. Kuo, "Disorder Effect on the Focus Image of Sonic Crystals in Air," *Physical Review E* **73**, 056615 (2006).
14. L. S. Chen, S. Li, T. F. George, C. H. Kuo and X. Sun, "Propagation of Surface Wave Pulses Over an Uneven Topographical Bottom," *Applied Physics Letters* **89**, 011905 (2006).
15. V. Karbushev, A. Semakov, V. Popov, I. Konstantinov, T. F. George and V. Kulichikhin, "Development of Polymer Composites Reinforced with Nanodiamonds and Clays," *Proceedings of the 12th European Conference on Composite Materials* (Biarritz, France, 2006), 5 pages.
16. R. R. Letfullin, C. Joenathan, T. F. George and V. P. Zharov, "Laser-Induced Explosion of Gold Nanoparticles: Potential Role for Nanophotothermolysis of Cancer," *Nanomedicine* **1**, 473 (2006).
17. A. V. Zhukov, M. V. Paliy, O. M. Braun and T. F. George, "Two-Stage Melting in Tribological Systems," *Physics Letters A* **361**, 437 (2007).
18. R. Letfullin, V. Zharov, C. Joenathan and T. George, "Nano-Photothermolysis of Cancer Cells," *SPIE Newsroom (Society of Photo-Optical Instrumentation Engineers)* DOI: 10.1117/2.1200701.0634-1-2 (2007) – http://newsroom.spie.org/x5983.xml.
19. L. Nánai, S. Szatmári, G. J. Taft and T. F. George, "On the Induction Period of Laser-Driven Thermochemical Processes," *International Journal of Theoretical Physics, Group Theory and Nonlinear Optics* **11**, 301-6 (2007).
20. S. Li, T. F. George, X. Sun and L. S. Chen, "Electric-Field-Induced Spin Accumulation in Polymer Light-Emitting Diodes" *Journal of Physical Chemistry B (Letters)* **111**, 6097 (2007).

21. G. P. Zhang and T. F. George, "Normal-Mode Selectivity in Ultrafast Raman Excitations in C_{60}," *Physical Review B* **73**, 035422 (2006).
22. G. P. Zhang and T. F. George, "Ellipticity Dependence of Optical Harmonic Generation in C_{60}," *Physical Review A* **74**, 023811 (2006).
23. G. P. Zhang, T, F. George, L. Assoufid and G. A. Mansoori, "First-Principles Simulation of the Interaction between Adamantane and an Atomic-Force-Microscope Tip," *Physical Review B* **75**, 035413 (2007).
24. G. P. Zhang and T. F. George, "Manifestation of Electron-Electron Interactions in Time-Resolved Ultrafast Pump-Probe Spectroscopy in C_{60}: Theory," *Physical Review B* **76**, 085410 (2007).
25. G. P. Zhang, "High Harmonic Generation in Atoms, Molecules and Nanostructures," *International Journal of Modern Physics B* **21**, 5167 (2007)
26. G. P. Zhang and T. F. George, "Origin of Ellipticity Anomaly in Harmonic Generation in C_{60}," *Journal of the Optical Society of American B* **24**, 1150 (2007).
27. H. Ramezani and G. A. Mansoori, "Diamondoids as Molecular Building Blocks for Nanotechnology," in *Molecular Building Blocks for Nanotechnology: From Diamondoids to Nanoscale Materials and Applications*, edited by G. A. Mansoori, T. F. George, L. Assoufid and G. P. Zhang (Springer, New York), *Topics in Applied Physics* **109**, 44 (2007).
28. R. Vajtai, B. Q. Wei, T. F. George and P. M. Ajayan, "Chemical Deposition of Organized Architectures of Carbon Nanotubes for Applications," in *Molecular Building Blocks for Nanotechnology: From Diamondoids to Nanoscale Materials and Applications*, edited by G. A. Mansoori, T. F. George, L. Assoufid and G. P. Zhang (Springer, New York), *Topics in Applied Physics* **109**, 188 (2007).
29. G. P. Zhang and T. F. George, "Theoretical Investigations in Retinal and Cubane," in *Molecular Building Blocks for Nanotechnology: From Diamondoids to Nanoscale Materials and Applications*, edited by G. A. Mansoori, T. F. George, L. Assoufid and G. P. Zhang (Springer, New York), *Topics in Applied Physics* **109**, 246 (2007).
30. G. P. Zhang, Y. Bai, W. Hübner, G. Lefkidis and T. F. George, "Understanding Laser-Induced Ultrafast Magnetization in Ferromagnets: First-Principles Investigation," *Journal of Applied Physics* **103**, 07B113 (2008).
31. G. P. Zhang and T. F. George, "Total Angular Momentum Conservation in Laser-Induced Femtosecond Magnetism," *Physical Review B (Brief Reports)* **78**, 052407 (2008).